

UDC 666.112.2:537.311.3

# ALLOWANCE FOR STRUCTURAL SPECIFICS IN A MODEL OF ELECTRIC CONDUCTANCE AND DIFFUSION OF LIQUATING ALKALI-SILICATE GLASSES

V. V. Samoteikin<sup>1</sup> and O. A. Gladushko<sup>1</sup>

Translated from Steklo i Keramika, No. 5, pp. 15–18, May, 2002.

Based on the drop model describing the heterogeneous structure of liquating glasses, an integrated expression is obtained for calculating the effective conductivity and the cation diffusion coefficient depending on the overall content of the alkaline oxide. The proposed model agrees with the experimental data for sodium and lithium silicate glasses.

The conductance of alkali-silicate glass rapidly grows with increasing alkaline oxide content, and in glasses capable of liquation (lithium and sodium-silicate glasses) this is attributed to a heterogeneous chemical composition of the medium in which the cation migrates [1–3]. It is established that the chemical heterogeneity of such glasses is related to the existence of areas with increased or decreased alkaline oxide content, and the mutual arrangement of these areas depends on the glass composition.

The results of studying the electric properties and structural specifics are interpreted as a prevalence of isolated and non-interconnected zones rich in alkaline ion, whose total content in glass is low, and gradual homogenizing of the glass structure as the content of alkaline ion increases [2, 3]. In the case of lithium silicate glasses it is accepted that the composition of the phase rich in lithium, whether continuous or dispersed in silica, approaches a disilicate [3].

Electrical properties were investigated in [3] for direct and alternating current, but the general discussion concerned mainly the results of measuring dielectric properties using the heterogeneous dielectric model. The present study considers the known results of measuring active resistance using the heterogeneous conductor model.

Let us represent a heterogeneous conducting medium as a homogeneous matrix of constant composition, in which spherical drops with another content of the alkaline ions are dispersed (the dispersed phase). Let us replace all the various sizes of these drops and all the possible distances between by the mean drop radius  $\delta$  and the mean distance between the drop centers  $2R$ . Then it is possible to draw an average sphere of radius  $R$  from the center of each averaged drop, and

the surface of this sphere will be located at a distance  $R$  from the center of the nearest drop. It is evident that the electrical properties of the medium depend on the conductivity of the parts comprising the sphere, and the effective conductance of the sphere coincides with the averaged conductance of the medium.

The problem of the effective conductivity of a heterogeneous sphere was solved by D. Maxwell [4], and this solution in the terms of conductivity and in the accepted designations has the following form:

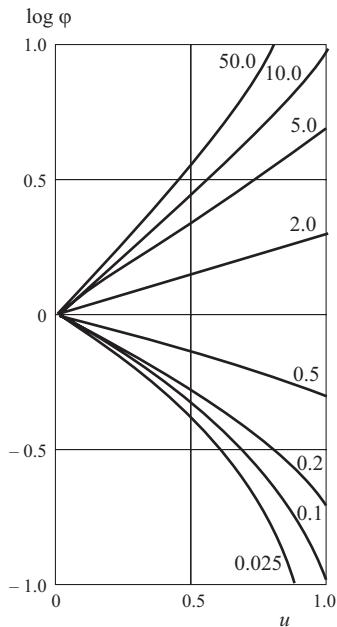
$$\sigma = \sigma_1 \left[ 1 + \frac{u}{\frac{1}{p-1} + \frac{1-u}{3}} \right] = \sigma_1 \varphi(u, p),$$

where  $p = \sigma_2/\sigma_1$ ;  $\sigma$ ,  $\sigma_1$ , and  $\sigma_2$  are, respectively, the conductances of the medium and of the outer ( $\delta \leq r \leq R$ ) and inner ( $r < \delta$ ) parts of the sphere ( $r$  means the coordinates of a point inside the sphere);  $u = (\delta/R)^3$ ;  $\varphi$  is a function of the parameter  $p$  and the volume part of the dispersed phase.

Thus, the parameter  $u$  is the volume part of the dispersed phase with electric conductance  $\sigma_2$ . It is easy to see that when this part decreases ( $u \rightarrow 0$ ), the conductance of the medium tends to the conductance of the matrix ( $\sigma \rightarrow \sigma_1$ ), and vice versa, with  $u \rightarrow 1$ ,  $\sigma \rightarrow \sigma_2$ .

Let us assume, as in [2, 3], that a modification of the bulk (volume-averaged) glass composition is accompanied by a redistribution of the volume parts of the matrix and the dissipated phase without a modification of the phase compositions, i.e., the value  $u$  may vary within a certain range of compositions, whereas the value of the parameter  $p$  remains

<sup>1</sup> Moscow State Night Metallurgical Institute, Moscow, Russia; Institute of Glass Joint-Stock Company, Moscow, Russia.



**Fig. 1.** Function  $\log \varphi (u, p)$  for different values of the parameter  $p$ .

constant. This can occur either due to a growing drop size  $\delta$ , or due to an increasing number of drops, i.e., a decreasing  $R$ . Various glass compositions of the same system can include several of such zones depending on the quantity of phases of the most probable composition, which are implemented in this particular system.

The relationship between  $u$  and the alkaline oxide concentration follows from the relationship

$$wR^3 = w_1(R^3 - \delta^3) - w_2\delta^3,$$

$w$ ,  $w_1$ , and  $w_2$  are the weight contents of the alkali oxide: the average content in the volume, in the matrix, and in the dispersed phase, respectively.

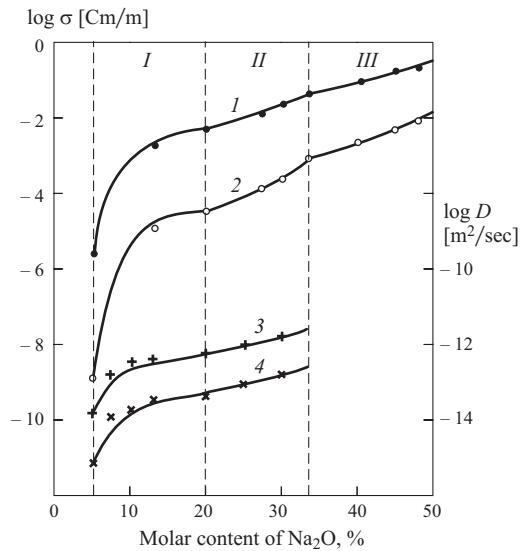
Hence

$$u = \frac{w - w_1}{w_2 - w_1}.$$

Thus, knowing the values  $\sigma_1$ ,  $u$ , and  $p$  for a particular system, the specified expression yields the value of electric conductance  $\sigma$  for any composition. Since the conductance is usually measured in the logarithmic scale, then

$$\log \sigma = \log \sigma_1 + \log \varphi (u, p).$$

The form of the function  $\log \varphi (u)$  for some values of the parameter  $p$  is given in Fig. 1. The function is positive at  $p > 1$  and is negative under a reverse relationship. In the first case a system with a low-conducting matrix and high-conducting inclusions is described. An increase in the alkaline oxide content in glass correlates with a linear growth of  $u$  and a rapid increase in  $\log \varphi (u)$ . At  $p < 1$ , the matrix has elevated conductivity and an increasing  $u$  is accompanied by



**Fig. 2.** Electric conductance and diffusion coefficients of sodium-silicate glass at temperatures of 300 (1, 4), 150 (2), and 415°C (3): 1 and 2)  $\log \sigma$ ; 3 and 4)  $\log D$ .

a more or less sharp (depending on the value of the parameter  $p$ ) drop of the function  $\log \varphi (u)$ . The increasing  $u$  in this case means a decreasing  $w$ .

Since the relationship between  $w$  and  $u$  is linear in both cases, the mutual location of the high- and low-conducting phases can be identified by analyzing the specifics of the behavior of the curve  $\log \sigma$  depending on  $w$ . If there are break points on this curves, i.e., if the curve slope  $\log \sigma (w)$  changes with a jump, the break points can be regarded as the boundaries of zones with different values of the parameter  $p$ . If, furthermore, the curvature sign changes at this boundary (i.e., a break point is at the same time a deflection point), the mutual arrangement of the high- and low-conducting phases is reversed.

At  $p > 1$ , the conductance value at the boundary can be regarded as the value  $\sigma_1$  for the zone to the right of the boundary and as  $\sigma_2$  to the left of the boundary, and at  $p < 1$ , vice versa, the value  $\sigma_1$  correlates with the zone on the left of the boundary.

The results of applying this model to lithium and sodium silicate glasses are shown in Figs. 2 and 3. The model uses experimental data on electrical conductance of sodium silicate glasses at temperatures 150 and 300°C for a wide range of compositions, i.e., from 5 to 48% (here and elsewhere molar content indicated) [5, 6] and the results of measuring electric conductance in lithium silicate glasses at 150°C for compositions containing from 8 to 40%  $\text{Li}_2\text{O}$  after different cooling conditions [2].

Based on the experimental dependence curves, the whole range of sodium silicate glass compositions can be divided into three segments: I) 5–20%; II) 20–33.3%, and III) 33.3–48%. The boundary between segments I and II is

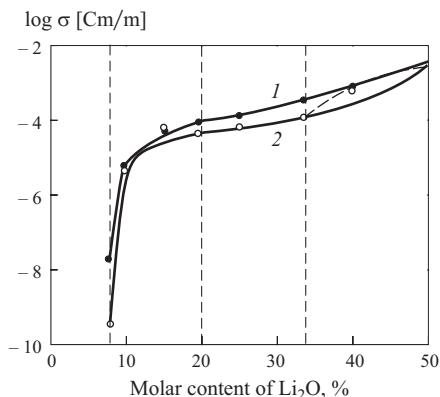


Fig. 3. Electric conductance of hardened (1) and annealed (2) lithium silicate glasses after heat treatment at 150°C.

determined by a deflection point corresponding to the  $\text{Na}_2\text{O}$  content equal to 20%. The boundary between segments *II* and *III* is determined by a break point (33.3%  $\text{Na}_2\text{O}$ ). The break point correlates with a  $\text{Na}_2\text{O}$  content equal to 33% in sodium silicate glasses is also described in the study by K. Blank [5], and its location does not depend on temperature in a wide interval (from 50 to 450°C).

The form of the  $\log \sigma$  dependence on the  $\text{Na}_2\text{O}$  content suggests that the low conducting phase within segment *I* is the isolated phase for this composition range. The low-conduction phase forms the matrix in segments *II* and *III*, and whereas this phase in segment *II* correlates with 20% alkali oxide, in segment *III* it correlates with disilicate. In a perfect case, the glass structure of the compositions corresponding to the boundary values (20 and 33.3%  $\text{Na}_2\text{O}$ ) should be homogeneous.

Table 1 lists the values of the parameters used in the calculation of the conductance of sodium and lithium silicate glasses (Figs. 2 and 3). It can be seen that the estimated curves satisfactorily describe the experimental regularities, even those obtained by different authors. The parameters  $p$  and  $\sigma$  were determined based on the data published by O. A. Mazurin [5] and V. K. Leko [2].

The study in [2] compares electric properties of lithium silicate glasses of the same composition, but with a different

thermal prehistory: some glasses were rapidly cooled after melting (hardening), others were annealed, and virtually all conductivity values in annealed samples are lower than in hardened samples. These measurements related to segment *III* allow for a dual interpretation.

In selecting the parameter  $p$  for hardened samples using the estimated curve, it is most logical to assume  $p > 1$ , similar to sodium silicate glasses (then  $p = 12.7$ , and extrapolation of this dependence to glass containing 50%  $\text{Li}_2\text{O}$  yields  $\log \sigma_2 = -2.43$ ). The condition of  $\log \sigma_2 < -2.43$  for hardened glasses at  $p > 1$  leads to  $p = 26$  and  $\log \sigma_2 = -2.60$ , but a significant discrepancy arises between the estimated and the experimental data at the point corresponding to a composition with 40%  $\text{Li}_2\text{O}$ . Assuming  $p < 1$  (then  $p = 0.038$ ,  $\log \sigma_1 = -2.60$ ,  $\log \sigma_2 = -4.00$ ; these values in Table 1 are in brackets and a possibility of such phase distribution in Fig. 3 is indicated in dashed lines), we accomplish a satisfactory approximation but contrast the annealed lithium silicate glasses to alkali-silicate glasses. The possibility of a final choice between these variants is limited by the fact that only two glass compositions correlate with the specified segment.

Considering that conductance in alkali-silicate glasses is determined by the mobility of the alkali cation and the latter also determines the diffusion  $D$  of the respective cation, one can expect a similar dependence of the diffusion coefficient of this cation on the glass composition.

Figure 2 represents the dependence  $\log D$  on the glass composition under two temperatures [6], and Table 2 lists the values of the parameters used to construct the estimation curves.

It can be seen from Fig. 2 that the general shape of the  $\log D$  vs. glass composition curve repeats the similar dependence for  $\log \sigma$ .

Based on the drop model for describing the heterogeneous structure of liquating glasses, an expression was obtained for the estimation of the effective conductivity value and the cation diffusion coefficient depending on the total content of the alkaline oxide. This model agrees with the experimental data for sodium and lithium silicate glasses.

According to this model, the presence of an inflection point on the curves of the  $\log \sigma$  or  $\log D$  vs. composition of the alkali-silicate glass indicates a modified distribution of

TABLE 1

Sodium silicate glass				Lithium silicate glass			
segment	$t, ^\circ\text{C}$	$\log \sigma_1$ [ $\Omega^{-1} \cdot \text{cm}^{-1}$ ]	$p$	segment	glass*	$\log \sigma_1$ [ $\Omega^{-1} \cdot \text{cm}^{-1}$ ]	$p$
<i>I</i>	150	-4.45	$10^{-4}$	<i>I</i>	Hardened	-4.11	$2.0 \times 10^{-4}$
<i>I</i>	300	-2.36	$10^{-3}$	<i>I</i>	Annealed	-4.32	$6.5 \times 10^{-6}$
<i>II</i>	150	-4.45	24.5	<i>II</i>	Hardened	-4.11	4.0
<i>II</i>	300	-2.36	5.2	<i>II</i>	Annealed	-4.32	2.1
<i>III</i>	150	-3.06	13.2	<i>III</i>	Hardened	-3.52	12.7
<i>III</i>	300	-1.34	8.7	<i>III</i>	Annealed	-4.00 (-2.60)	26 (0.038)

\* Heat treatment at 150°C.

TABLE 2

Segment	<i>t</i> , °C	$\log D_1$ [m <sup>2</sup> /sec]	<i>p</i>
<i>I</i>	300	–13.30	0.018
	415	–12.23	0.030
<i>II</i>	300	–13.30	4.5
	415	–12.23	4.0

the alkali oxide in glass (the sign of the parameter *p* changes), whereas a break point indicates only a modification of the parameter *p* and the composition of the phases forming a continuous matrix and isolated inclusions.

Indeed, within the interval of compositions with a low overall content of the alkali oxide (segment *I*), the area with an increased content of the cation simply connected, i.e., it forms a matrix in which isolated inclusions rich in silica are located. As the overall content of the alkali oxide in the glass grows, the volume content of these inclusions decreases, and the composition corresponding to the boundary between segment *I* and *II* satisfies the homogeneity condition (*u* = 0).

Within the composition range with a medium content of the cation (segment *II*), inclusions containing 33.3% Na<sub>2</sub>O are found in the matrix containing 20% alkali oxide, and the share of these inclusions grows with increasing total content

of the alkali oxide in the glass, until the structure again becomes homogeneous near the boundary between segment *II* and segment *III*. The same is repeated within segment *III*, in which the composition of the inclusion rich in the cation presumably correlates with glass containing 50% Na<sub>2</sub>O.

Thus, the dispersed phase in the considered glasses containing less than 20% alkali oxide is a low-alkali phase, and the disperse phase in glasses with a high overall content of alkali oxide is highly alkaline.

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